The Reduction of Copper Oxide by Carbon Monoxide and the Catalytic Oxidation of Carbon Monoxide in Presence of Copper and of Copper Oxide

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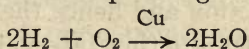
HOWARD ALGERNON JONES

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THE REDUCTION OF COPPER OXIDE BY CARBON MONOXIDE AND THE CATALYTIC OXIDATION OF CARBON MONOXIDE IN PRESENCE OF COPPER AND OF COPPER OXIDE

The mechanism of even simple chemical reactions and of simple catalytic actions is by no means so fully investigated as could be desired, nor is it possible to state definitely in many cases how such reactions occur. Reasoning by analogy is apt to lead to quite erroneous conclusions and such conclusions tend to retard chemical progress. The truth of these statements may be very well illustrated by detailed investigations of such apparently simple reactions as the reduction of oxides by various reducing gases and the catalytic oxidation of such gases in presence of metallic oxides or their reduced metals. A simple statement of a reaction by chemical formulae such as:—

$$CuO + H_2 = Cu + H_2O$$
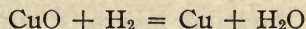
fails to reveal the complexities of the reduction process as the recent study of this reaction by Pease and Taylor[1] has shown. Nor does the corresponding equation

$$2H_2 + O_2 \xrightarrow{Cu} 2H_2O$$

give any real picture of the mechanism of the catalytic change.

The following investigation attempts to extend our knowledge of these simple processes by a thorough study of the reduction of copper oxide by carbon monoxide and of the catalytic combination of carbon monoxide and oxygen in presence of copper oxide and of reduced copper. It will be seen that these reactions show striking similarities in certain aspects to the corresponding reactions with hydrogen. At the same time there are marked and fundamental differences, which, as will be shown, are of great importance in processes,

[1] Pease and Taylor: Jour. Am. Chem. Soc., **43**, 10, 2179 (1921).

such as the preferential combustion of carbon monoxide in hydrogen, having important technical possibilities.

An investigation of the reduction of copper oxide by carbon monoxide has been carried out by Wright, Luff and Rennie.[1] Carbon monoxide generated by treating potassium ferrocyanide with sulphuric acid and purified by caustic soda, silver nitrate and sulphuric acid was passed at a constant rate through a U-tube containing weighed amounts of copper oxide obtained by calcining the nitrate. The temperature of the U-tube was maintained constant at various fixed temperatures by means of vapor baths and the amount of reduction determined by weighing the U-tube after a lapse of time. Experiments were carried out over a range of temperature from 84° to 185°. Measurements were also made of the amount of reduction of copper oxide in sealed tubes, filled with carbon monoxide and maintained at constant temperature for periods up to 6 hours. Using the continuous flow method, an initial period of "incubation" was observed during which no measurable amount of reduction took place, this period varying in duration inversely with the temperature. The reduction appeared to start at some particle of oxide (as evidenced by the appearance of copper nuclei at this point) and was propagated from particle to particle through the mass. The amount of reduction and hence the rate of carbon dioxide formation over any definite time interval increased very rapidly after the start (induction period), passed through a maximum and as the oxide was converted to metal became again immeasurably small.

In an earlier paper by Wright and Luff[2] the following statement is made: "In the course of some other experiments of the same kind, it was noticed that when the carbon oxide was not purified from small quantities of admixed air, the amount of carbon dioxide collected greatly *exceeded* that corresponding to the loss of weight; thus in two experiments the following numbers were obtained:—

[1] Wright, Luff and Rennie: Jour. Chem. Soc., **35**, 475 (1879).
[2] Wright and Luff: Jour. Chem. Soc., **33**, 1 (1878).

Time of exposure	Oxygen removed, calculated from carbon dioxide found, that originally present being 100 percent	Oxygen removed, calculated from the loss in weight
(1) 90 minutes	155.0 percent	71.9 percent
(2) 220 minutes	113.0 percent	72.0 percent

whence it is evident that, either the partially reduced oxide acted catalytically in causing combination between the free oxygen and the carbon oxide in the gaseous mixture, or the nearly reduced oxide took up the free oxygen and was then again reduced in virtue of the reactions:

$$Cu_xOy + O = Cu_xO_{y+1}$$
$$Cu_xO_{y+1} + CO = Cu_xOy + CO_2$$
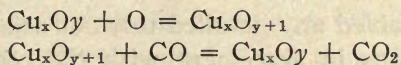
thus forming more carbon dioxide than that corresponding to the difference between the original oxygen in the cupric oxide employed and that left associated with the copper after the action was completed."

Beyond the observation that a mixture of carbon monoxide and air, when passed over partly reduced copper oxide, gives an abnormally large amount of carbon dioxide when calculation is made on the basis of the oxygen content of the copper oxide, the above authors arrived at no definite conclusions as to the mechanism of such action. A thorough and more detailed study of these points might, it was thought, assist in explaining this mechanism.

In claiming protection for the process of preferential combustion of carbon monoxide in hydrogen, Harger and Terry[1] cite the use of copper and of copper oxide in addition to various other metals and oxides.

E. K. Rideal[2] in a study of the preferential nature of the above process concluded that in presence of copper oxide, a mixture containing 14 percent carbon monoxide, 11.5 percent oxygen and 74.5 percent hydrogen gave a ratio of 0.466 carbon monoxide to 1 hydrogen by volume burned when passed at

[1] Harger and Terry: Brit. Pat., **127**, 609 (1917).
[2] E. K. Rideal: Jour. Chem. Soc., **115**, 993 (1919).

a rate of 33 cc per minute at 280°. At lower temperatures the ratio $CO:H_2$ of the burnt gases shows a continuous increase. Rideal furthermore suggests that the two oxidation processes may be related to one another by the equation

$$\frac{-\dfrac{d\,C_{co}}{dt}}{-\dfrac{d\,C_{H_2}}{dt}} = \frac{(CO)}{(H_2)(O_2)^{1/2}}$$

Various assumptions were made as to mechanisms which would result in this ratio and also as to the adsorptions of the several gases concerned. None of the theories as to mechanism received any detailed test nor are the assumptions as to adsorptions in agreement with the recently published data of Taylor and Burns[1] relative to the metal catalysts nor with the data of Dr. A. F. Benton[2] on metallic oxides. In the latter work it has been shown that strong preferential adsorption of carbon monoxide occurs with but small adsorptions of oxygen and hydrogen by active oxide masses. Some evidence as to reaction mechanism will be adduced in this communication.

Due to the increased importance of the problem of the removal of small percentages of carbon monoxide from air, the Chemical Warfare Service of the U. S. Army during the late war made a series of investigations in order to develop suitable catalysts for this work.[3] As a result of this war work, Lamb, Scalione and Edgar[4] have made use of a catalyst consisting of 60 percent manganese dioxide and 40 percent cupric oxide called Hopcalite, to burn carbon monoxide preferentially when present in concentrations up to 1 percent in hydrogen. Their communication appeared subsequent to the completion of this work and they conclude that the results obtained are

[1] Taylor and Burns: Jour. Am. Chem. Soc., **43**, 6, 1273 (1921).

[2] Benton: Ibid., **45**, 887 (1923).

[3] Lamb, Bray and Frazer: Jour. Ind. Eng. Chem., **12**, 213 (1920); Rogers, Piggot, Bahlke and Jennings: Jour. Am. Chem. Soc., **43**, 9, 1973 (1921); Merrill and Scalione: Ibid., **43**, 9, 1982 (1921).

[4] Lamb, Scalione and Edgar: Ibid., **44**, 4, 738 (1922).

not in conflict with the computations put forward by E. K. Rideal, relative to the simultaneous oxidation of carbon monoxide and hydrogen. The mechanism of preferential catalytic oxidation of carbon monoxide in admixture with hydrogen is not discussed by them.

It is suggested[1] that the mechanism of the catalytic oxidation of carbon monoxide in concentrations up to 5 percent in air may possibly be explained by a chemical theory. This theory is based on the alternate reduction and oxidation of any one or possibly all of the various oxides as used in mixtures by the above authors in order to obtain suitable catalysts. They further suggest that the oxide upon which the catalytic activity of the mixture depends is not reoxidized by oxygen fast enough to maintain its catalytic action when present alone and hence the function of the other oxide or oxides is to increase the velocity of the reoxidation of the active constituent of the catalyst mixture.

Experimental

A sketch of our apparatus is shown in Figure 1. Electrolytic oxygen from tank (A) was passed through heated palladized asbestos in the tube (B) to convert the small percentage of hydrogen in the gas to water, thence through a phosphorus pentoxide drying tube (C). From (C), the pure dry oxygen was passed through a Nichrome tube filled with graphite and resting in a furnace (D) maintained at 1050–1100° C. The carbon monoxide thus formed was led through a heated silica tube (E), containing copper turnings, to convert any traces of oxygen present at this point to carbon dioxide, through the soda-lime towers (F) to remove carbon dioxide, through the flow-meter (H), the phosphorus pentoxide in (K) and finally, into the electrically heated furnace (L) which contained the copper oxide. The furnace consisted of two co-axial glass tubes, the inner one containing the copper

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[1] Rogers, Piggott, Bahlke and Jennings: Jour. Am. Chem. Soc., **43**, 9, 1973 (1921).

oxide charge while the outer one was wrapped on the outside with nichrome wire and covered with magnesia pipe covering thus serving as a heating jacket. Temperatures were always read on a mercury-filled thermometer with the bulb directly in contact with the oxide charge. The thermometer passed out through the outer jacket at the top. Near the bottom of the outer jacket was sealed a T-tube (M), through which the gases were admitted, passed up between the outer and inner tube and down through the oxide in the inner tube. An electrolytic generator (N), was used for obtaining the small quantities of oxygen used in the work. This oxygen was passed through heated palladized asbestos in silica tube
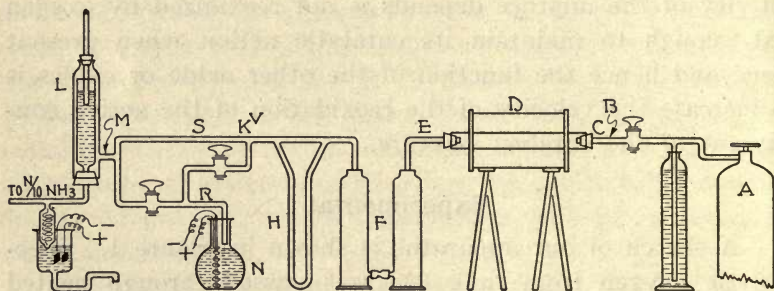

Fig. 1

(P), over phosphorus pentoxide in (R) and admitted to the carbon monoxide stream at the T-tube (M). When carbon dioxide was wanted, the necessary amount of oxygen gas was admitted to the carbon monoxide at point (V) and burned to carbon dioxide over heated copper in silica tube (S).

Rates of reduction were measured by determining the rate of carbon dioxide formation. This was accomplished in a portion of the work by means of an apparatus reported by Rideal and Taylor.[1] They measured the fall in conductivity of one-two hundredth normal lime water caused by absorption of carbon dioxide which precipitates calcium carbonate. Since we were dealing with much higher con-

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[1] Rideal and Taylor: The Analyst, **44**, 89 (1919).

centrations of carbon dioxide the heavy precipitate of calcium carbonate might clog the absorption system and collect around the electrodes, thereby creating a disturbing influence on conductivity measurements. For this reason, we took advantage of the fact that one-tenth normal ammonia water has a much lower conductivity than one-tenth normal ammonium carbonate and used one-tenth normal ammonia for the absorbing medium. The effluent gases from the furnace (L) were passed co-currently with a constant flow of
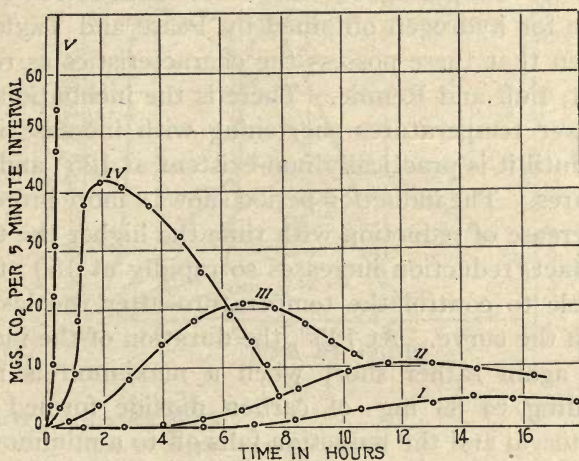

Fig. 2

Curve I, reduction at 80°
Curve II, reduction at 90°
Curve III, reduction at 100°
Curve IV, reduction at 125°
Curve V, reduction at 150°

calibrated ammonia water through a spiral condenser coil and into the conductivity cell maintained at constant temperature. In some of the experiments, the carbon dioxide was absorbed by soda-lime and weighed.

Rates of reduction are expressed throughout in terms of milligrams of carbon dioxide formed in a 5-minute interval. The rate of flow of carbon monoxide was maintained constant at 50 cc per minute. Samples of 5 cc apparent volume of

copper oxide weighing within a few tenths of 10 g were always employed. Since the containing tube was 2.5 sq. cm. in cross section, this gave a layer of oxide about 2 cm deep. An imported copper oxide intended for organic analysis (8–10 mesh) was used.

It has been shown[1] that the initial temperature at which reduction of metallic oxides by carbon monoxide occurred, was consistently lower in the cases investigated, to the initial temperature at which hydrogen causes reduction. This is verified by comparing our curves for reduction in Figure 2 with those for hydrogen obtained by Pease and Taylor.[2] It will be seen that these possess the characteristics as reported by Wright, Luff and Rennie. There is the incubation period at the lower temperatures shortening with increase in temperature until it is practically non-existent at 125° and higher temperatures. The induction period shows a more pronounced rate of increase of reduction with time the higher the temperature; in fact, reduction increases so rapidly at 150° that we were unable to control the temperature after the last point marked on the curve. At 125°, the duration of the induction period is again rather short when a maximum is reached corresponding to 83 mg of carbon dioxide formed per 5-minute interval and the reduction falls off to a minimum from this point. If all the carbon monoxide passed had been converted to carbon dioxide, the rate would have corresponded to 450 mg in 5 minutes.

The characteristics of the reduction were made clear by examination of numerous samples in the various stages of the same. The reduction appeared to start (as evidenced by the appearance of the red speck of copper) at some particle in the lower half of the charge at the lower temperatures (below 125°). At 125° and 150°, the reduction generally commenced at some point near the middle of the charge, while at still

[1] Wright and Luff: Jour. Chem. Soc., 33, 1, 504 (1878); Fay, Lane, Seeker and Ferguson: Poly. Eng., 10, 72 (1910).

[2] Pease and Taylor: Jour. Am. Chem. Soc., 43, 10, 2179 (1921).

higher temperatures, the initial action would usually be observed in the first layer of oxide where contact with the carbon monoxide was first made.

Effect of Copper

It was shown[1] that copper is an auto-catalyst for the reduction of copper oxide by hydrogen by virtue of the increased area of copper-copper oxide interface formed; the reduction occurring most readily and for the most part at this
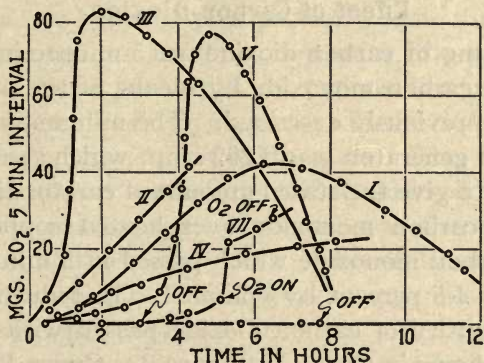

Fig. 3

Curve I, reduction at 100°
Curve II, effect of copper on reduction at 100°
Curve III, reduction at 125°
Curve IV, effect of 20 mg equivalent of oxygen on reduction at 25°
Curve V, effect of 20 mg carbon dioxide on reduction at 125°
Curve VI, effect of 20 mg equivalent of oxygen on reduction at 100°
Curve VII, effect of 20 mg equivalent of oxygen on reduction at 100°

point. It seemed desirable to try this same effect of copper on the reduction by carbon monoxide. This was done with a layer of freshly reduced granules placed on top of the oxide and reduced at 100°. The result is shown graphically by Curve II, Figure 3. Curve I, Figure 3 represents the reduction by carbon monoxide of pure copper oxide at 100°. A comparison of the curves shows that the incubation period is practically eliminated, it being brief though measurable

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[1] Pease and Taylor: Jour. Am. Chem. Soc., **43**, 10, 2179 (1921).

normally. An examination of this sample after reduction had proceeded as far as indicated showed that the initial action had begun at the top of the charge in contact with the copper but reduction had also set in at the bottom of the charge so that the copper-copper oxide interface area was greater than usual, thus explaining the slightly greater rate of reduction in Curve II. It had been noted that ordinarily the top layer of oxide was last reduced at 100° so that this was evidence of the auto-catalytic nature of the reduction.

Effect of Carbon Dioxide

Twenty mg of carbon dioxide per 5-minute interval were added to the carbon monoxide by means of the arrangement of apparatus previously described. The milliammeter reading of the oxygen generator was 0.292 amp. which generated sufficient oxygen to give the stated amount of carbon dioxide when passed with carbon monoxide over heated copper. In the 250 cc of carbon monoxide which passed in 5 minutes, this is equivalent to 4.5 percent by volume. The reduction at 125° with this quantity of carbon dioxide passed with the carbon monoxide is shown in Curve V, Figure 3. Curve III, Figure 3 represents the normal reduction at 125°. A comparison of these curves shows that whereas normally there is no measurable incubation period at 125°, the presence of this small quantity of carbon dioxide in the carbon monoxide causes an incubation period of about one hour while the time of induction is also lengthened 2 hours. Pease and Taylor have shown that a very small quantity of water vapor inhibits the reduction of copper oxide by hydrogen most probably as a result of an adsorbed, protective layer of water vapor on the surface of the copper oxide which effectively prevents the formation of copper nuclei at this temperature. Dr. A. F. Benton has found in this laboratory that carbon dioxide is adsorbed by copper oxide though in all probability it is not so strongly adsorbed as water vapor. That carbon dioxide has little effect on the reduction at the copper-copper oxide interface is plainly evident since the carbon dioxide was run

during the entire experiment and once the formation of the copper nuclei was well started, the reduction follows the regular curve. The effect, therefore, is probably to form a slight protective film on the copper oxide surface and thus retard the primary reaction, i. e., the formation of copper nuclei.

Effect of Oxygen

Since carbon monoxide and hydrogen, with more than sufficient oxygen to burn completely all the carbon monoxide present, is passed over copper oxide as a preferential combustion catalyst, we believed that probably some important data could be obtained to assist in explaining the mechanism of this reaction by experiments at various temperatures with a known percentage of oxygen present in the carbon monoxide passed through the copper oxide mass. The effect on the reduction of copper oxide by carbon monoxide containing about 2.6 percent oxygen by volume was therefore tried at 80°, 90°, 100°, 125°, and 150°. The milliammeter setting was again 0.292 amp. This is oxygen equivalent to 20 mg of carbon dioxide per 5-minute interval. The curves for the reduction of copper oxide at 80° and 90° by carbon monoxide containing this amount of oxygen are not included since the effect is exactly similar to that at 100°, the time of passage of the gases being 8 and 9 hours, respectively, for these temperatures.

The effect of oxygen on the reduction at 100° is shown by Curve VI, Figure 3. Curve I, Figure 3 represents the straight reduction at this temperature. The gases were passed for 7.5 hours at 100° and the rate of carbon dioxide formation never exceeded 0.4 mg which is within the experimental error, so that the curve is drawn as a straight line along the X axis, i. e., the reduction is immeasurable over this period. Furthermore, an examination of the sample at the end of the experiment showed no visible copper nuclei present. The effect of oxygen on the reduction at 125° is shown by Curve IV, Figure 3. Curve III, Figure 3 is the normal reduction at this temperature. We find from Curve IV, Figure 3 that the carbon

dioxide formation attains a rate of 7 mg per 5-minute interval after 2 hours has elapsed, whereas normally, the rate passes through a maximum corresponding to 83 mg of carbon dioxide per 5-minute interval in this time. The straight reduction is about 90 percen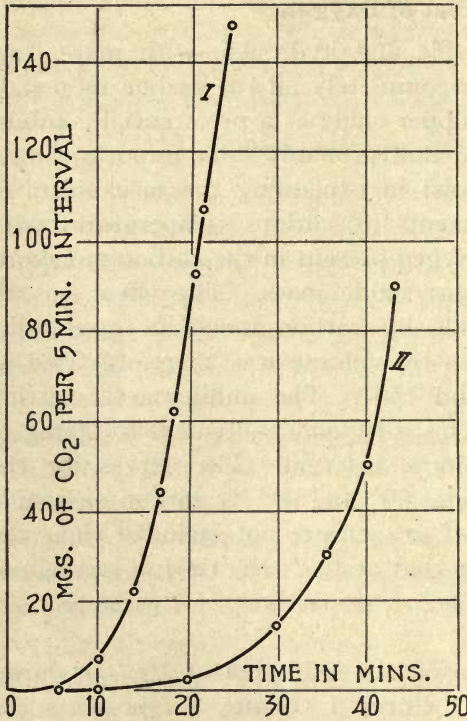t completed at the end of 8 hours, while with this small amount of oxygen, the curve does not pass through a maximum and only attains a 22 mg rate per 5-minute interval in this time. The sample showed on examination at the end of the run that copper nuclei were present in only very small amount in several particles at the center of the charge. Curve II, Figure 4 shows the effect of oxygen on the initial stages of the reduction at 150° while Curve I, Figure 4, is the straight reduction. The reduction begins normally at 150° as soon as pure carbon monoxide comes in contact with the copper

Fig. 4

Curve I, reduction at 150°
Curve II, effect of 20 mg equivalent of oxygen
on reduction at 150°

oxide but the effect of oxygen is to cause over a ten minute incubation period which, though short, is nevertheless measurable. Reduction in absence of oxygen attains a rate of 148 mg when 25 minutes have elapsed while with oxygen present, the rate is only 8 mg in the same elapsed time. Again, an examination of samples showed fewer visible copper nuclei

present at the end, when oxygen was passed with the carbon monoxide.

In order to throw more light on the mechanism of the effect of oxygen on the reduction, an experiment was performed in which a 20 mg equivalent of oxygen was passed with the carbon monoxide over a charge of copper oxide for 3 hours at 100°; the oxygen being shut off at the end of this time and the rate of reduction measured to determine the effect on the induction period. When the rate of reduction was found to be increasing in the usual manner, the oxygen was again turned in, the rate of carbon dioxide formation having attained a value of 6 mg in 5 minutes. If the effect of oxygen on the reduction by hydrogen[1] were taken as a criterion, our curve should show a sudden drop to a minimum at this point. However, on taking into consideration the adsorption values of carbon monoxide and hydrogen on copper as determined by Taylor and Burns along with the earlier observations of Wright and Luff as stated previously, we believed that the effect of oxygen with carbon monoxide at this point might possibly give results which are entirely different from those of oxygen with hydrogen. Taylor and Burns showed that, with reduced copper, the adsorption of carbon monoxide is strong, while that of hydrogen is of a much lower order comparable with that of oxygen. Hence, in a carbon monoxide-oxygen mixture, it would be anticipated that the carbon monoxide would be preferentially adsorbed. The results of Pease and Taylor indicate that in a hydrogen-oxygen mixture, the oxygen is adsorbed at the copper-copper oxide interface. The actual result which we obtained is shown in Curve VII, Figure 3. The rate of carbon dioxide formation was found to rise from 6 mg to 21.5 mg immediately the oxygen was admitted and the curve rose gradually from this point. This extremely interesting and fundamentally important result led us to try the same effect of oxygen on the reductions at 90° and 100° with the oxygen turned in at 3 different stages of the same in each

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[1] Pease and Taylor: Jour. Am. Chem. Soc., **43,** 10, 2179 (1921).

case. These results are shown graphically by Curves I and II, Figure 5. To gather more definite information as to the amount of oxygen in the effluent gases from the furnace chamber in the course of one of these experiments, the gases from the carbon dioxide recording instrument were passed first through soda-lime, over phosphorus pentoxide, and finally over hot copper turnings and the resultant carbon dioxide taken up in a U-tube containing soda-lime with a phosphorus
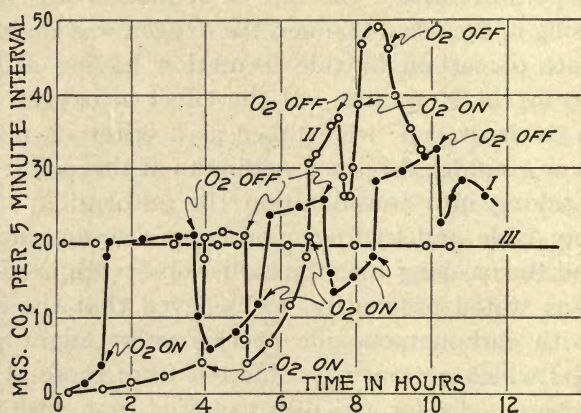

Fig. 5

Curve I, effect of 20 mg equivalent of oxygen added after start of reduction at 90°

Curve II, effect of 20 mg equivalent of oxygen added after start of reduction at 100°

Curve III, effect of 20 mg oxygen passed with carbon monoxide over reduced copper oxide

pentoxide tube following next the soda-lime. These two U-tubes were weighed at frequent intervals during the experiment at 100° while the oxygen was on. Their total gain in weight represents the carbon dioxide equivalent of the oxygen coming through the furnace chamber unchanged. These data are presented in Column IV, Table I.

We may consider Curve II, Figure 5 as a general example of the effect of oxygen on the reduction. When the reduction rate was 4 mg, a 20 mg equivalent of oxygen was turned

in and the rate rose immediately to 21 mg. During this first period, while oxygen was on, there was oxygen equivalent to 1.5 mg carbon dioxide coming through unchanged. The difference, or the equivalent of 18.5 mg carbon dioxide, had reacted. In both the latter periods of "oxygen on" at 100°, the entire amount of oxygen admitted had reacted. It is evident therefore, that even in the presence of the small amount of copper produced by the time the reduction rate corresponds to 4 mg per 5-minute interval, $\frac{18.5}{20.0} \times 100$ or 92 percent of the oxygen was converted to carbon dioxide. At this stage of the reduction of the copper oxide, very few nuclei of copper are discernible. When more nuclei are present, that is, when the reduction rate has reached 20 mg, carbon dioxide per 5-minute interval, the oxygen conversion is quantitative.

Table I is self-explanatory and is derived entirely from the curve and the data in Column IV.

TABLE I

I	II	III	IV	V	VI
Period of "oxygen on"	Reduction rate at start of period	Reduction rate at end of period	Amount of un-converted oxygen	Initial reading with "oxygen on"	Last reading with "oxygen on"
First	4.0 mg	4.3 mg	1.5 mg	21.0 mg	21.3 mg
Second	21.0 mg	26.5 mg	0.00 mg	31.2 mg	37.3 mg
Third	39.0 mg	38.0 mg	0.00 mg	47.0 mg	47.0 mg

NOTE:—The rates are all expressed as mg CO_2 per 5-minute interval.

It may be seen from Curve II, Figure 5 that when the oxygen is admitted for the first time, the rate of reduction is 4 mg carbon dioxide per 5-minute interval. Since 18.5 mg equivalent of the oxygen admitted is converted to carbon dioxide, we find that the rate of reduction of the *original* copper oxide falls from 4 mg to a value of 2.5 mg carbon dioxide per 5-minute interval. Similarly, at the end of the oxygen run

the rate of reduction of the original oxide is 2.8 mg carbon dioxide per 5-minute interval, instead of 4.3 mg which is the first reading after turning off the oxygen. In the second period of oxygen admission, the value of 21 mg carbon dioxide per 5-minute interval rises to 31.2 mg immediately the oxygen is admitted. Again, knowing that the 20 mg equivalent of oxygen is quantitatively converted to carbon dioxide, we see that the rate of reduction of the *original* oxide falls from 21 to 11.2 mg carbon dioxide per 5-minute interval. The rate of reduction of the *original* oxide reaches a value of 17.3 mg carbon dioxide per 5-minute interval at the end of this period of oxygen admission, while the reduction occurs at a 26.5 mg. rate immediately the oxygen is turned off. At the start of the third period, the reading is 39 mg carbon dioxide per 5-minute interval. When the oxygen is in and quantitatively converted to carbon dioxide, the reading is 47 mg carbon dioxide per 5-minute interval. This gives a value of 27 mg for the reduction of the *original* oxide or a falling off in this value of 12 mg when the oxygen is admitted. We see further that the rate of reduction attains a maximum while the oxygen is in and falls off rapidly when the oxygen is turned off.

As stated previously, Pease and Taylor found that at temperatures below 200°, the effect of oxygen turned in, while reduction of copper oxide by hydrogen was under way, was to inhibit the reduction process. At the same time, the amount of water vapor formed per 5-minute interval fell off to a very low value, a few mg at most. The conclusion to be drawn from a comparison of our results with carbon monoxide and oxygen over partly reduced copper oxide with those observed by the above authors using hydrogen and oxygen warrants special consideration.

In both cases, it is possible to pass mixtures of hydrogen with a small percentage of oxygen present and of carbon monoxide containing a small percentage of oxygen over the copper oxide mass for an indefinite period without measurable quantity of reaction product, either water vapor or carbon dioxide, being formed. This has been demonstrated with hydrogen-

oxygen mixtures over copper oxide at 150° and with a carbon monoxide-oxygen mixture at 100°. Hence, the explanation for the fundamentally different results obtained must be sought in the action of the reduced copper on the two mixtures.

Therefore, a sample of the copper oxide was completely reduced to metal at 150° and the 20 mg equivalent of oxygen turned in at 200°. The initial reading showed that the entire amount of oxygen was being quantitatively catalysed to carbon dioxide. The temperature was then allowed to drop in steps of 10° each until finally, and much to our surprise, we were effecting complete catalysis of the oxygen in the mixture with no heat on the furnace, the temperature of the copper maintaining itself at 37° C by virtue of the heat of the reaction. In the next experiment, the oxygen was admitted when the copper was at room temperature, 25°. Again, the oxygen was quantitatively converted to carbon dioxide from the start and the temperature rose to 37°, the gases being passed for many hours with the same effect throughout.

Through a study of the mechanism of the catalysis of hydrogen-oxygen mixtures, Pease and Taylor conclude that their results are best explained on the basis of a chemical action or the reaction may be said to proceed through an intermediate compound stage. They present definite evidence of the alternate oxidation and reduction of the copper to give as end products, water vapor and metallic copper, though an oxide of copper is no doubt formed in an intermediate stage of the process.

In a hydrogen-oxygen mixture containing a few percent of oxygen, the oxygen is not quantitatively converted to water vapor when passed over copper until a temperature of 200° is reached. In a similar mixture of carbon monoxide and oxygen, the oxygen passed is quantitatively converted to carbon dioxide at temperatures as low as our arrangement of apparatus permitted, namely 37° C. We subsequently showed that this reaction went extremely rapidly, *even at* 0° C.

We believe that a suitable explanation could be obtained for our totally different result with a carbon monoxide-oxygen

mixture by a consideration of the relative values of carbon monoxide and hydrogen on copper as determined by Taylor and Burns. We thought it best however, to attempt a direct experimental check on the possibilities of alternate oxidation and reduction of the copper which would be direct evidence either for or against an explanation of the mechanism of the catalysis of carbon monoxide-oxygen mixtures over copper on the basis of an intermediate chemical compound stage. This was done in the following manner.

Carbon monoxide was passed over reduced copper at room temperature at the usual 50 cc per minute rate. Twenty mg equivalent of oxygen was then admitted and the quantitative conversion to carbon dioxide allowed to proceed for 5 hours, the temperature maintaining itself at 40°. The carbon monoxide was shut off at the end of this time and pure dry oxygen gas allowed to pass over the copper maintained at 40° for several days. It had been noted previously that active copper, reduced at low temperatures gradually became oxidized on long standing at room temperature in air. After this treatment, the carbon monoxide alone was passed for a period of three hours without the least measurable amount of carbon dioxide being formed at 40°. The same quantity of oxygen as before was admitted at this point and passed for several hours without a trace of carbon dioxide being formed. On shutting off the oxygen, and raising the temperature rapidly to 180°, the surface was again reduced to copper as evidenced by the amount of carbon dioxide formed while the temperature was being raised. The reduction did not attain measurable proportions until the temperature had reached 90°–100°. By the time 180° was reached, the rate of carbon dioxide formation had fallen to practically zero once more, the time necessary to raise the temperature being only twenty minutes. The carbon monoxide was passed for a time at this higher temperature to insure complete reduction, after which the heating current was turned off and the sample allowed to attain 40° once more. The 20 mg equivalent of oxygen was admitted and the initial reading showed quantitative con-

version to carbon dioxide. When this constant result was noted for a period of several hours, the experiment was discontinued.

This experiment is presented in a graphic form in Curve I, Figure 6. It is apparent therefore that this result is very direct evidence against a theory of intermediate compound formation, i. e., alternate oxidation and reduction of the copper to explain the mechanism of the catalytic combination of carbon monoxide and oxygen over copper.

Fig. 6

Hoping to obtain more evidence which would assist in explaining the mechanism of the reaction:

$$2CO + O_2 \xrightarrow{\text{Cu}} 2CO_2$$
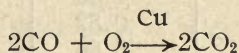
we next made measurements of this reaction by a static method. A large reaction tube was filled with (8–10) mesh copper oxide, sealed to a capillary T-tube and this in turn connected with a Toepler pump and a measuring burette by means of a three way cock. The free end of the T-tube was sealed to one arm of a mercury manometer. The copper oxide was then reduced in situ with hydrogen at a temperature of 200° and this sample used for reaction velocity measurements. It was found, however, that *the reaction was practically complete in less than 1 minute* after admitting the carbon monoxide-oxygen mixture in a stoichiometric ratio to the catalyst maintained at a temperature of 0° C. Obviously, no data could be obtained from such an active catalyst so, after many trials of various forms of copper oxide using higher temperatures
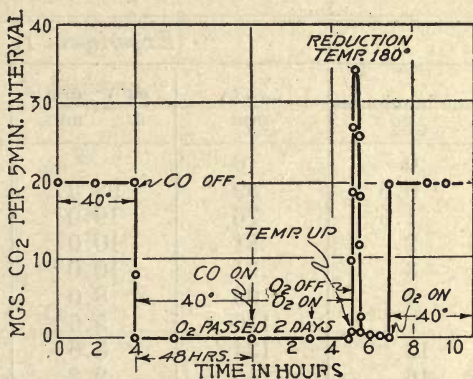
of reduction, a measurable reaction was obtained as follows. A wire form of copper oxide was reduced with hydrogen at a temp. of 300–350° and subsequently subjected to a long

TABLE II

Time in minutes	$-dp$ in mm	$\frac{dx}{dt}$ in $\frac{mm}{min.}$	Initial p.p. Carbon Monoxide	Initial p.p. Oxygen
Experiment 1.				
0	0		480	235
0.6	59	98.3		
1.5	76	19.0		
2	81	10.0		
3	91	10.0		
4	99	8.0		
7	116	5.66		
12	134	3.6		
16	145	2.2		
21	155	2.0		
26	163	1.6		
31	170	1.4		
37	176.5	1.08		
41	181	1.12		
46	186	1.00		
57	195	0.82		
66	201	0.66		
76	208	0.70		
86	213	0.50		
96	218	0.50		
Experiment 2.				
0	0		224	107
0.6	7	11.7		
2	11	3.0		
5	18	2.33		
10	26	1.6		
16	33	1.17		
33	46	0.77		
55	59	0.59		
65	63	0.40		
80	68	0.333		
97	73	0.29		
110	77.5	0.35		
125	81	0.233		

Experiment 3.

0	0		462	225
1.1	5	4.54		
3	10	2.63		
6	14	1.33		
14	23	1.12		
19	27.5	0.90		
24	31.0	0.70		

Experiment 4.

0	0		506	245
0.85	80	94.1		
1.7	96	18.8		
3	112	12.3		
5	130	9.0		
10	158	5.6		
14	171	3.25		
18	179	2.0		

period of heating at 450–500° C in hydrogen (18 hours). By this treatment, we obtained a copper surface sufficiently low in activity to enable us to obtain measurements of the reaction to be studied at the boiling point of benzene.

The equation for the reaction

$$2CO + O_2 = 2CO_2$$
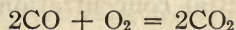
shows that when the reaction occurs there appear only two molecules of carbon dioxide to replace two molecules of carbon monoxide and one of oxygen so that there is a volume diminution of one-third. The progress of the reaction was then made clear by using a constant volume method in which the fall in pressure was measured on the manometer.

For purposes of calculation, the free space of the system was measured with nitrogen and an adsorption isotherm of carbon monoxide measured on this relatively inactive copper at a temperature of 80° C. Measurements had previously been obtained on the adsorption isotherms of both carbon monoxide and carbon dioxide at several temperatures on a much more active copper.

The preceding data in Table II were obtained in several

typical experiments on the reaction velocity measurements of $2CO + O_2 = 2CO_2$ over copper at 80° C.

Expt. 1 was made using the partial pressures of carbon monoxide and oxygen as recorded in the table. It may be noted that an amount of carbon monoxide somewhat greater than that called for by the stoichiometric equation was used.

Expt. 2 was performed for the purpose of studying the effect of carbon dioxide on the rate of the reaction. This was accomplished by using approximately half the amount of the mixed gases in the second case and comparing the initial rate of reaction observed with that measured in the first experiment when the values for the concentrations of carbon monoxide and oxygen had reached the initial values of these same as used in Expt. 2.

The curves presenting these results in graphic form are shown in Figure 7. Curve I represents Expt. 1; Curve II, Expt. 2, and so on. The values dp are plotted against elapsed time throughout.

From a comparison of Curves I and II, it will be seen that the values for the initial concentrations as used in Expt. 2 were attained after 10 minutes elapsed time in Expt. 1. In the ensuing 86 minutes, the system experienced a fall in pressure of 90 mm in Expt. 1 while in the first 86 minutes Expt. 2 showed only 70 mm decrease in pressure. This may be observed also by a comparison of the dx/dt values in the table for these experiments.

Since it was thought that the velocity of the reaction should be the same or even more rapid in Expt. 2, owing to the initial absence of carbon dioxide and since experiment showed the reverse to be true, we concluded that in all probability the copper was undergoing oxidation without subsequent reduction of the oxide formed even though there was a slight excess of carbon monoxide present.

To confirm this belief, Expt. 3 was performed. Here the ratio of carbon monoxide to oxygen was the same as in

Expts. 1 and 2 while an initial pressure of the mixture comparable to that in Expt. 1 was used.

It was apparent after a short time had elapsed that the velocity of the reaction had again decreased. From the curves, we see that in 24 minutes the system experienced a decrease in pressure of 31 mm in Expt. 3 while in Expt. 1, a decrease of 160 mm was observed in the same elapsed time and Expt. 2 where only half the concentration of gases was used decreased 40 mm in pressure over the same time interval.

This was then additional evidence of the decrease in the velocity of the reaction in successive experiments. In order that we could state positively whether the copper was undergoing oxidation without subsequent reduction of the oxide, the copper was subjected to treatment with hydrogen at 200° when it was noted that marked amounts of water collected in the capillary tubes. After thoroughly pumping out, a stoichiometric ratio of $2CO : O_2$ was used to obtain the data as tabulated under Expt. 4, Table II and plotted on Curve IV, Figure 7.
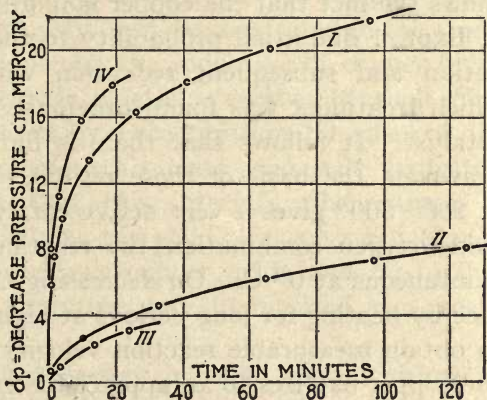
Fig. 7

Reaction Velocity Measurements

Curve I, a stoichiometric mixture of carbon monoxide oxygen over copper at 80° using one atmosphere

Curve II, a half atmosphere of a stoichiometric mixture at 80°

Curve III, stoichiometric mixture using one atmosphere at 80°

Curve IV, effect of treating copper surface with hydrogen at 200° after experiments represented in Curves I–III. One atmosphere of a stoichiometric mixture used in this curve

It is evident from a comparison of Curve IV with Curves I, II and III in Figure 7, that the surface of the copper has be-

come activated by this treatment with hydrogen. A decrease in pressure of 179 mm. in 18 minutes is observed in Expt. 4 as against a decrease of 149 mm in the same elapsed time in Expt. 1 while in Expt. 3, which was also performed before the treatment with hydrogen at 200°, the same time interval indicated a decrease in pressure of only 26 mm.

A comparison of Curve IV with Curve I in Figure 7 further shows the fact that the copper is more active in Expt. 4 than in Expt. 1 due in all probability to the low temperature oxidation and subsequent reduction with hydrogen at 200°, which treatment was found previously to give a very active catalyst. It follows that there is but one conclusion to be drawn on the basis of these results. Copper oxide reduced at 200°–300° gives a very active catalyst for the carbon monoxide-oxygen combination; the reaction being practically instantaneous at 0° C. On decreasing the activity of this surface by heating for long periods at high temperatures in order to obtain measurable reaction velocity data, it is found that the copper oxidizes to an appreciable extent at 80° C in presence of excess of carbon monoxide. In successive experiments without subsequent reduction of the oxide formed, the activity of the catalyst, and hence the rate of the reaction is found to decrease rapidly. When this surface layer of oxide, which may be observed by the darkened color of the catalyst, is reduced at 200° with hydrogen, the copper becomes more active with each successive treatment so that finally one arrives at the starting point with a very active copper catalyst, i. e., the carbon monoxide-oxygen combination reaches equilibrium in less than 1 minute at 0° C.

Conclusions

The importance of the interface between the two phases copper-copper oxide in the reduction of copper oxide by carbon monoxide has been demonstrated in the present work. It has been shown that low temperature reduction of copper oxide by carbon monoxide is negligible until copper nuclei are established in the copper oxide mass. Subsequent re-

action then occurs at the boundary copper-copper oxide as may be observed by the ever increasing area of the red copper extending outwards from the original nuclei. The amount of carbon dioxide produced per unit of time as a result of such reduction at the interface, increases steadily with increasing extent of interface, attains a maximum and then steadily diminishes as the reduction of the oxide is completed. This phenomenon of the activity existing at the copper-copper oxide interface had previously been demonstrated in the study made by Pease and Taylor on the reduction of copper oxide by hydrogen. It is another case of a variety of such phenomena recently indicated by Langmuir[1] in the cases of dissociation involving calcium carbonate and salt hydrates. Langmuir's conclusion that this interface phenomenon is general for reactions involving two solid phases is strengthened by our observations on copper-copper oxide and by further examples found in the literature and summarized in a recent article by Taylor.[2]

Carbon dioxide when present in small concentrations in carbon monoxide has been shown to exert a retarding effect on the primary reaction of the reduction of copper oxide, i. e., the formation of copper nuclei. As previously stated, carbon dioxide is markedly adsorbed by copper oxide. There is the possibility therefore, that the carbon dioxide is adsorbed to form a slight protective film on the copper oxide surface which would satisfactorily account for the retardation effect observed. The lengthening of the time of induction observed probably finds explanation in the fact that carbon dioxide is measurably adsorbed by copper at the copper-copper oxide interface at which point the reduction process has been shown to occur.

Oxygen present in small concentration has been shown to produce a pronounced retardation of the reduction process.

[1] Langmuir: Trans. Faraday Soc., Sept. (1921); Jour. Am. Chem. Soc., **38**, 2263 (1916).

[2] H. S. Taylor: Jour. Franklin Inst., **194**, 1 (1922).

The effect of oxygen on the reduction at low temperatures is probably to oxidize the copper atoms to copper oxide as quickly as they are formed, thus suppressing the spread of the copper-copper oxide interfaces so that, under the conditions chosen, the reduction does not assume measurable proportions. As the temperature is raised, however, the rate of formation of copper nuclei exceeds the rate of re-oxidation of the copper atoms by the small amount of oxygen present so that reduction increases gradually with time. The evidence obtained, along with many visual observations, lends support to the view that the mechanism in this case is one of alternate reduction of the copper oxide, forming carbon dioxide and copper, and regeneration of the copper oxide by oxidation of the copper.

The experiments with oxygen admitted after the copper nuclei formation was well under way pointed to a possible fundamental difference between the mechanism of carbon monoxide-oxygen combination over copper and that obtaining over copper oxide. A consideration of these experiments along with those subsequently performed with completely reduced copper definitely established this fundamental difference. The combination of carbon monoxide and oxygen over copper oxide is found to be a relatively slow process, the mechanism being one of alternate reduction and oxidation at an interface. In contrast to this relatively slow process for the combination of carbon monoxide with oxygen, is that taking place practically instantaneously over a reduced active copper. In this case, it has been established very definitely that the mechanism is certainly not one of intermediate compound formation, i. e., alternate oxidation and reduction, but rather the oxidation of an adsorbed layer of carbon monoxide on the copper surface. This conclusion aids in explaining the observation that a small amount of oxygen, initially present in the carbon monoxide, may completely suppress the spread of the copper-copper oxide interface at certain temperatures while oxygen, admitted after copper nuclei have been formed in sufficient amount, combines directly with the carbon monoxide, adsorbed on the copper, to give the

greatly increased quantities of carbon dioxide observed under these conditions.

It has been shown by Taylor and Burns that hydrogen is very markedly adsorbed by nickel. As stated previously, they have also noted marked adsorption of carbon monoxide on copper while the adsorption of oxygen is negligible on the same metal. From a consideration of some unpublished data obtained in this laboratory, Pease and Taylor conclude that the mechanism for the combination of hydrogen and oxygen over reduced nickel is best explained on the basis of the adsorption theory of contact catalysis. This reaction also occurs at room temperature under conditions from which they conclude that here again the oxygen combines directly with the adsorbed oxidizable gas, i. e., hydrogen. As noted previously, Pease and Taylor from a study of the catalytic combination of hydrogen and oxygen over copper, conclude that an explanation for the mechanism of this reaction is based on intermediate compound formation, i. e., alternate oxidation and reduction. Taylor and Burns have also shown that the adsorptions of both hydrogen and oxygen on copper are small.

This striking parallelism to be observed in the mechanism obtaining in the cases of carbon monoxide-oxygen combination over copper and hydrogen-oxygen combination over nickel when considered along with the totally different mechanism observed in the combination of hydrogen-oxygen mixtures over copper, lend especial weight to the conclusions drawn by Taylor and Burns from a study of the adsorption of gases by various metal catalysts.

As a result of the static measurements carried out in this work, the conclusion is drawn that oxygen is a "poison" in the combination of carbon monoxide and oxygen over copper. Poisons are now classified in heterogeneous catalytic work as either permanent or transitory. So called "permanent poisons" usually are found to react chemically with a catalyst reducing its activity continuously and progressively with extended use in presence of the poison.

Transitory poisons in gas reaction are most generally

to be explained on the basis of preferential adsorption of the poison from the gas mixture, even though this poison is present in only minute quantities. The adsorption is, however, reversible and the poisoning effect disappears either wholly or in part on removal of the transitory poison from the gas mixture.

On the basis of this classification and the data obtained by us, oxygen may be said to be a "permanent poison" for the carbon monoxide-oxygen combination over copper. In this case, copper oxide is formed, the activity of the catalyst decreases rapidly and regeneration of the copper, by reduction of the oxide, is necessary to restore the activity. This is entirely analogous to the permanent poisoning of an iron catalyst in ammonia synthesis by formation of iron sulphide when sulphur compounds are present in the gases used. In this case, it is necessary to oxidize the sulphide and then regenerate the metal by reduction of the oxide.

As a result of some static experiments on the velocity of carbon monoxide-oxygen combination over copper oxide at 184–218°, we conclude that concordant results are unattainable in successive experiments. The mechanism for this reaction has been shown to be one of alternate reduction and oxidation. The velocity of the reaction shows a steady increase in successive experiments due, in all probability, to the reduction proceeding more rapidly in each successive case at a constant temperature.

Summary

1. The reduction of copper oxide by carbon monoxide has been shown to be an auto-catalytic process, copper being the auto-catalyst; the reduction occurring at a copper-copper oxide interface.

2. The retarding effects of carbon dioxide and oxygen on the primary reaction of the reduction process, i. e., the formation of copper nuclei, have been pointed out.

3. The mechanism for the combination of carbon mon-

oxide-oxygen mixtures over copper oxide has been shown to be alternate reduction and oxidation of the copper oxide.

4. The mechanism for the combination of carbon monoxide-oxygen mixtures over copper has been shown to be the oxidation of an adsorbed layer of carbon monoxide.

5. It has been established that oxygen is a "permanent poison" in the combination of carbon monoxide with oxygen over copper.

The writer desires to express his very sincere appreciation for the active co-operation and many helpful suggestions rendered to him in the course of this work by Professor Hugh S. Taylor.

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